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BOMBARDMENT INDUCED
PHOTOCONDUCTIVITY AND OPTICAL ABSORPTION
IN MAGNESIUM OXIDE

Harold R. Day

Office of Naval Research

TECHNICAL REPORT NO. 13

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DEPARTMENT OF PHYSICS
UNIVERSITY OF MISSOURI
COLUMBIA

BOMBARDMENT INDUCED PHOTOCONDUCTIVITY AND
OPTICAL ABSORPTION IN MAGNESIUM OXIDE

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Technical Report No. 13

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Abstract

Crystals of magnesium oxide have been colored by irradiation with ultraviolet light, x-rays, high energy electrons and neutrons. The spectral distribution of optical absorption has the form of a gradually increasing tail extending from the visible region to the far ultraviolet upon which are superimposed several absorption bands. Photoconductivity in single crystals of magnesium oxide was measured by a d.c. method using a vibrating reed electrometer. The spectral distribution of photoconductivity is characterized by a gradually rising tail with superimposed peaks at 2.1, 3.7, and 4.8 eV, corresponding to known optical absorption bands. A photoconductivity band was found at 1.2 eV which has not been detected by optical absorption measurements. Irradiation of the crystals by ultraviolet light causes an enhancement of the photoconductivity subsequently measured in the 1.2 and 2.1 eV bands. The enhancement effect reaches a saturation level which is independent of the intensity of the ultraviolet light and which is a measure of the density of imperfections in the crystal lattice. The ultraviolet activated region can be displaced by an electric field in such a direction as to indicate that the charge carriers are holes in the valence band. Bombardment by Van de Graaff electrons produces an enhancement of photoconductivity which is unstable at room temperature. Neutron irradiation of the crystals gives rise to a thermally unstable enhancement of photoconductivity throughout the spectrum and also causes an increase in the level of saturation of the ultraviolet activation. The latter increase is stable at room temperature and indicates that the neutron irradiation produces new lattice defects. This effect saturates with increasing neutron flux. An estimate of the density of lattice defects can be made from the photoconductivity. An energy level model is proposed to explain the various photoconductivity bands and the enhancement and saturation effects.

I INTRODUCTION

Single crystals of magnesium oxide may be colored by irradiation with ultraviolet light¹, x-rays², neutrons and high energy electrons^{3,4}. Measurements of the spectral dependence of the optical absorption of the colored crystals have revealed several absorption bands in the visible and ultraviolet regions superimposed upon a gradually rising "tail" which extends over the entire spectrum and increases to only about 20 cm^{-1} at 200 m μ or 6.2 ev, the limit of measurement. There is good agreement between the absorption measurements performed by the writer and the published results of the other investigators¹⁻⁴. Absorption bands corresponding to those produced by irradiation have also been created⁵ by the direct addition of excess magnesium and oxygen to the crystal lattice. Previous attempts^{2,3,6} to find photoconductivity associated with this optical absorption have been unsuccessful. However, by the refinement of the techniques and the use of more sensitive current detecting apparatus, it has been possible to measure

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1. J.H. Hibben, Phys. Rev. 51, 530 (1937)
 2. J.P. Molnar and C.D. Hartman, Phys. Rev. 79, 1015 (1950)
 3. C.A. Boyd, D. Rich, and E. Avery, Atomic Energy Commission Report MDDC - 1508 (1947)
 4. C.M. Nelson and P. Pringsheim, Argonne National Laboratory Progress Report ANL - 4232 (2nd. quarter 1948)
 5. H. Weber, Zeitschrift fur Physik 130, 392 (1951)
 6. W.W. Tyler and R. L. Sproull, Phys. Rev. 83, 548 (1951)

the spectral dependence of photoconductivity in magnesium oxide single-crystals.

II EXPERIMENTAL APPARATUS

Most of the samples were plates on the order of one millimeter thick and one centimeter square which had been cleaved from larger crystals obtained from two sources. One group was supplied by the Norton Company⁷ and the other group was grown at this laboratory⁸. Aquadag electrodes were painted on opposite faces of crystals and were air dried at room temperature. The samples were mounted between spring clips on Teflon insulators in an airtight box containing a dish of calcium chloride as a drying agent. Desiccation was found to be essential because of high leakage currents caused by surface moisture. A quartz window was provided in the side of the box to permit the entrance of the irradiating wavelengths. In the visible and near infra-red regions, a tungsten filament projection lamp served as the light source, a 100 watt, type H-4 mercury arc was used in the near ultraviolet and a 1000 watt type H-6 mercury arc was used in the far ultraviolet. After passing through a Gaertner quartz monochromator the light was focused by means of a system of front surface mirrors onto the edge of the sample. Provision was made for using a thermopile to monitor the

7. The Norton Company, Niagara Falls 5, New York

8. These crystals were grown by Mr. H. F. John

intensity of the light at each wavelength setting. An electric field was placed across the crystal by means of an external battery. The resulting photocurrent was determined by passing it through a high resistance and measuring the potential drop which it produced by means of an Applied Physics Corporation vibrating reed electrometer. The highest resistance used was 10^{12} ohms and the electrometer would measure a potential of 10^{-4} volt so that currents as low as 10^{-16} amperes could be measured by the constant deflection method.

III EXPERIMENTAL RESULTS

1. Characteristics of Photoconductivity

The observed photocurrents were superimposed on a dark current of the order of 10^{-15} amperes which could be balanced out by a bucking voltage in the electrometer. The increase of current produced by illumination was called the photocurrent and it was found to be a linear function of the intensity of the light and of the electric field strength up to 14,000 volts/cm, the limit of measurement. It was also found that the photocurrent at a given wavelength and light intensity did not depend on whether the light was distributed over the whole edge of the crystal or focused on only a narrow region, as long as the total power received by the sample remained unchanged. When a narrow region in the center of a crystal was illuminated by ultraviolet light a current was produced which, after an initial decrease by a factor of about two, was constant

over a period of many hours. The mechanism whereby constant d. c. photocurrents can be produced by the illumination of only part of a crystal is not yet understood *. Because of the linear dependence of photocurrent upon intensity and electric field strength, the data were reduced to units of induced photoconductivity per unit optical power striking the crystal. No correction was made for the intensity of light which was not absorbed by the crystal since in the extreme case the correction amounted to only a factor of three at the longest wavelengths and was less than the estimated uncertainty in measurement at the shorter wavelengths. Since the photoconductivity ranged over several decades, this correction would add little to the interpretation of the results

The photoconductivity spectrum contains several bands which are shown in Fig. 1. The maxima of these bands occur at 1.2, 2.1, 3.7, and 4.8 ev, the latter three corresponding closely to optical absorption bands which were found in the previous investigations. Since photoconductivity

* A series of experiments was carried out to investigate this matter. It seems certain that true d. c. currents are being observed and that light scattered at the crystal surfaces and within the crystal is not sufficient to cause the observed photocurrents. No increase in photocurrent is observed when the light strikes the electrodes yet an experiment to be described later indicates a distance-of-travel of the charged particles of only 10^{-3} cm in a field of 1000 volts per cm. It is possible that the ever present dark current, although usually small, may have some bearing on this mechanism.

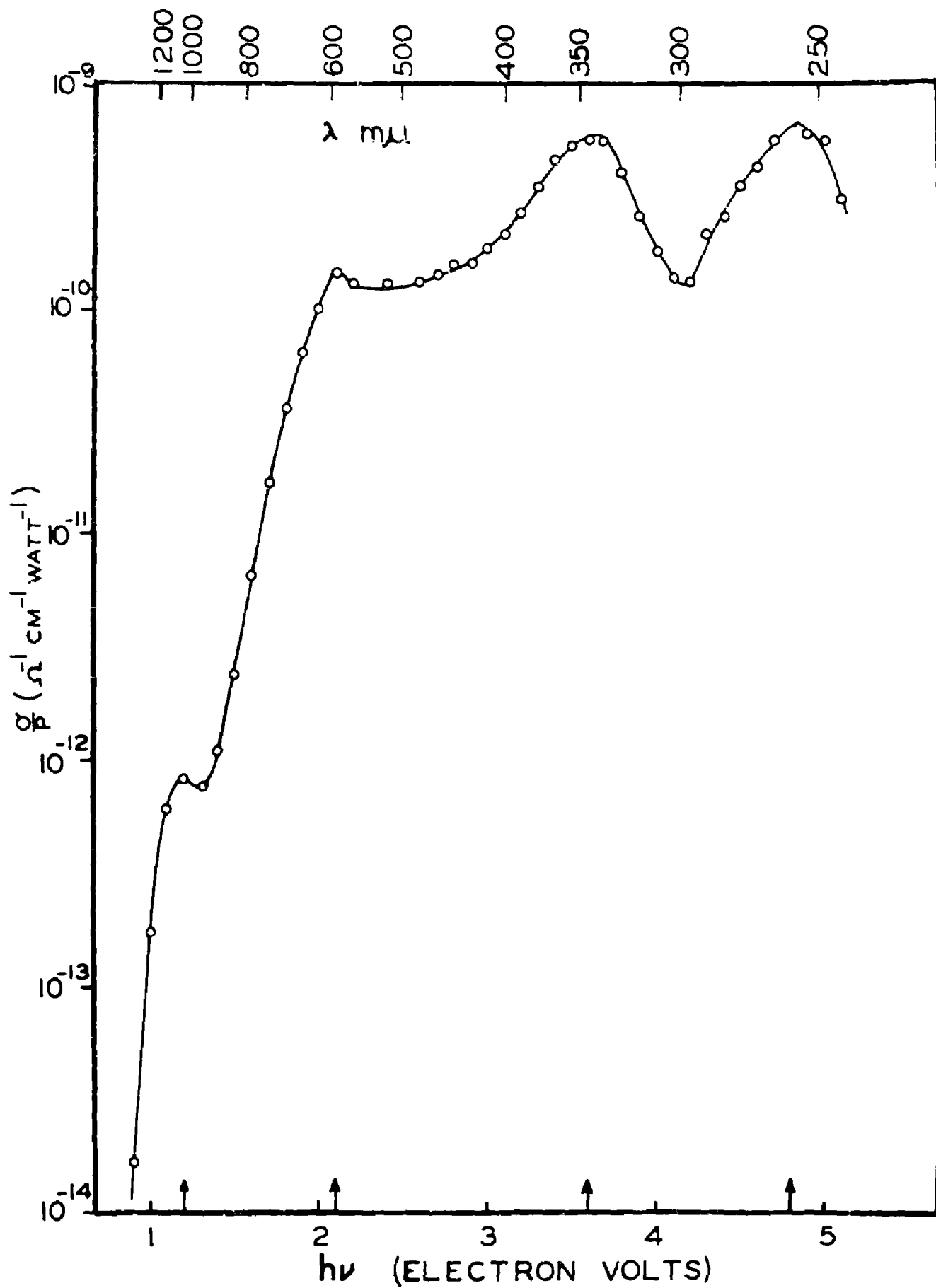


FIG. I

is a more sensitive measurement than optical absorption, it is understandable that the band at 1.2 ev has not been detected by absorption studies.

2. Ultraviolet Irradiation

Freshly cleaned crystals exhibited a photoconductivity spectrum similar to curve A of Fig. 2. The gradual rise and the shoulder at 580 m μ or 2.1 ev is characteristic of all photoconductivity spectra observed for magnesium oxide. The 580 m μ band suggests the presence of an energy level situated in the forbidden band so that a transition of 2.1 ev can produce free charge carriers, either in the conduction band or the valence band. An experiment to be described later has shown that the charge carriers arising from this transition are holes in the valence band; thus the associated energy levels are located 2.1 ev above the top of that band. It is believed that this photoconductivity band corresponds to the optical absorption band which occurs at very nearly the same wavelength and which causes the characteristic visible coloration of the crystals after irradiation. Curve B of Fig. 2 represents the level of photoconductivity in the same crystal after it had been irradiated for eight hours with ultraviolet light at 312 m μ . This treatment produced an increase by a factor of nearly a thousand in the photoconductivity at 2.1 ev and reveals the new band at 1050 m μ or 1.2 ev. The photocurrents in this region had

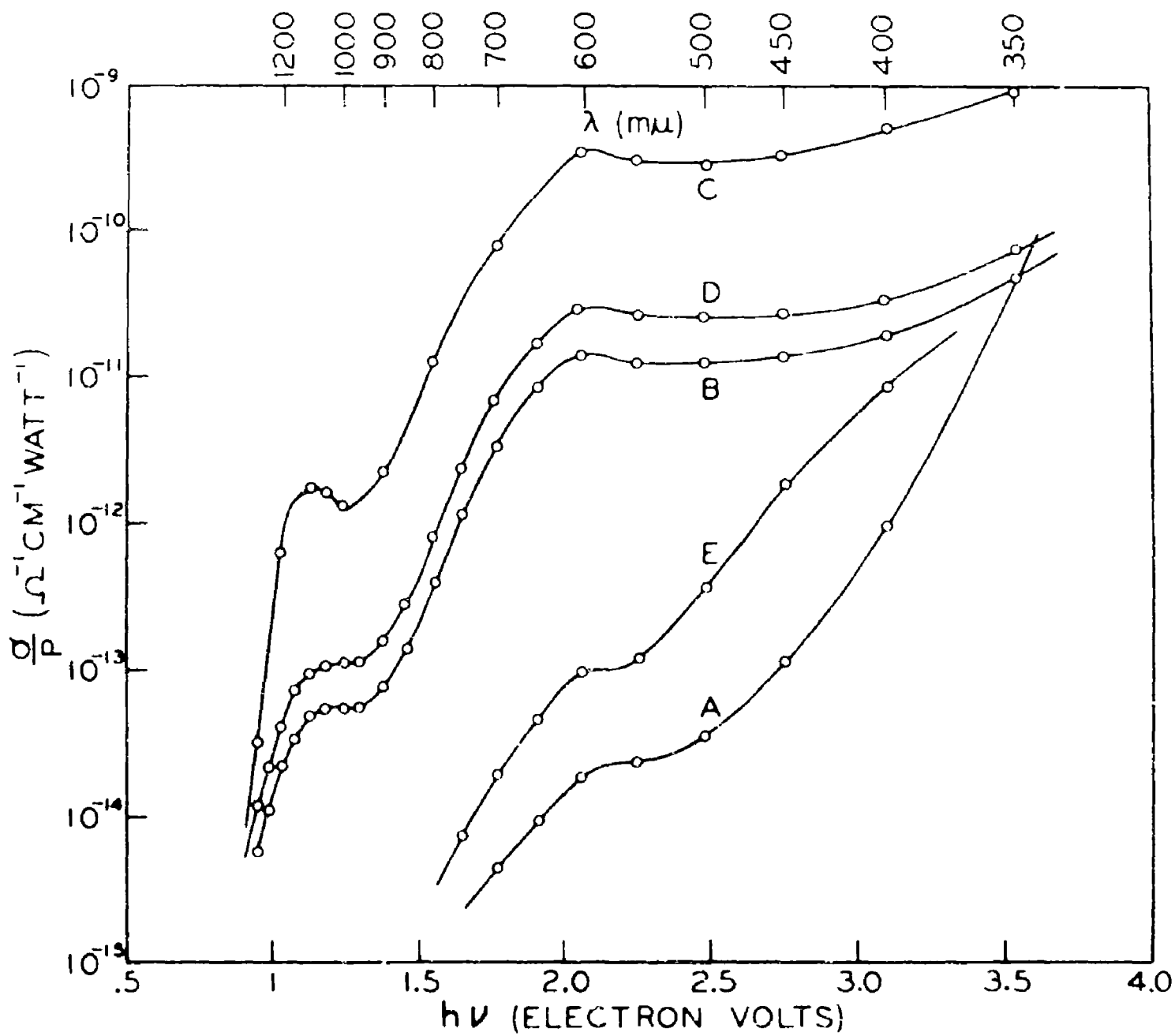


FIG. 2

previously been so small that they were beyond the range of the detecting instruments. The photocurrent at 312 mμ, the wavelength of irradiation, decreased by a factor of two during the first few minutes of the irradiation after which it remained constant. The enhancement of photoconductivity in the visible and infra-red regions of the spectrum by irradiation with ultraviolet light, and the decrease in the photoconductivity at the wavelength of irradiation correspond closely to the shift in the optical absorption spectrum which can be produced⁴ in a similar manner. This effect strongly suggests the transfer of electrons from one type of energy level to another in a manner similar to the process which is believed to occur in alkali halides⁹.

The dependence of the enhancement of photoconductivity upon the time of irradiation is shown in Fig. 3. The ultraviolet irradiation was interrupted for brief intervals during which the photocurrent produced by light of 580 mμ was recorded. It is apparent that the enhancement had nearly reached saturation after 160 minutes and with this ultraviolet intensity of 12 μ watts no further increase was observed after three hours of irradiation.

It was also found that if a crystal which previously had been activated by ultraviolet light was irradiated for a long time with yellow

9. N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals, Second Edition, p. 129 (Oxford University Press, London, 1948)

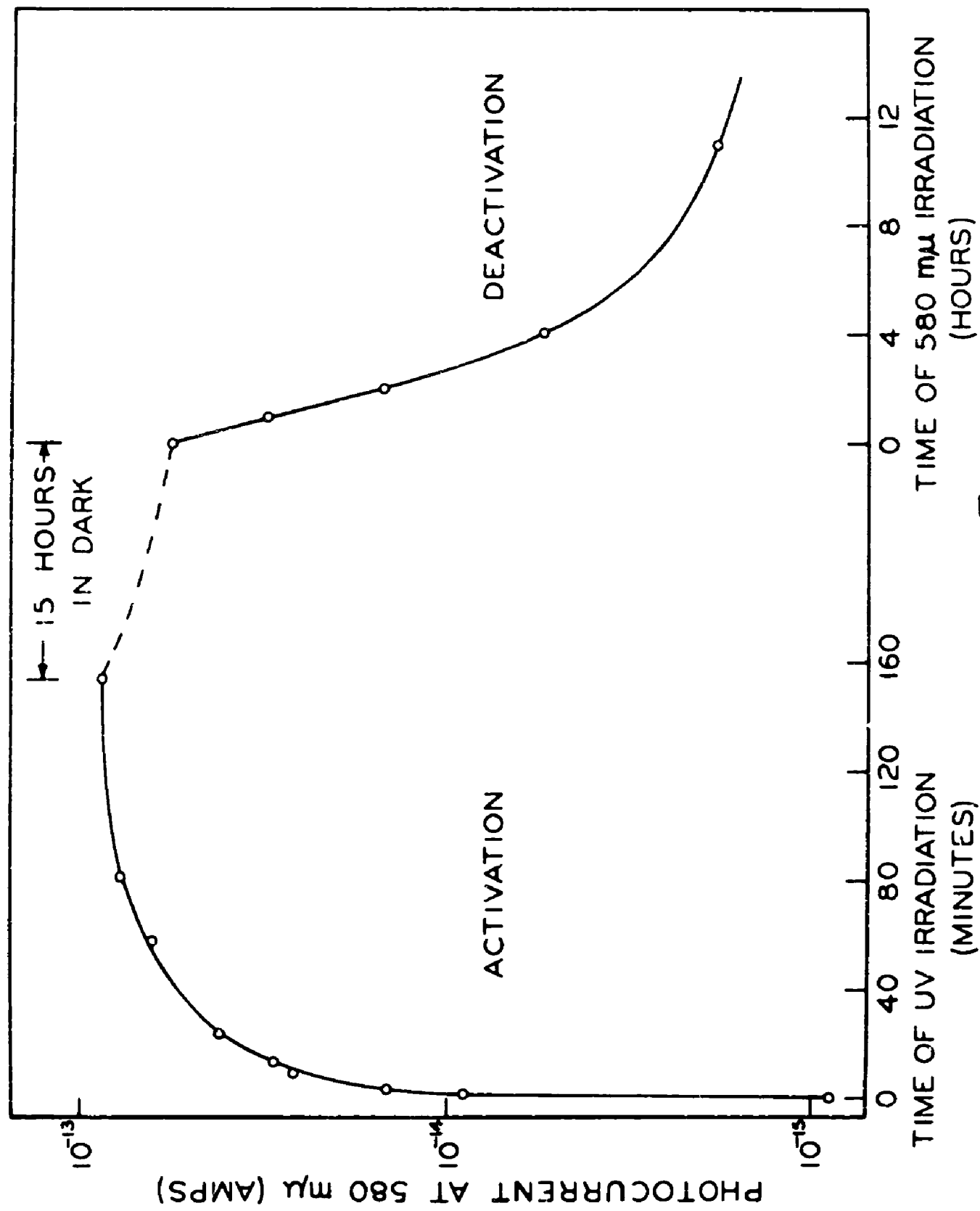


FIG. 3

light in the 580 m μ band, a decay was produced in the photoconductivity at all wavelengths above 350 m μ . This decay is shown in the right hand side of Fig. 3 where the photocurrent at 580 m μ is plotted as a function of the time of irradiation by 39 μ watts of light at that wavelength. The rate of decay was greater with more intense light. In later experiments, where a very rapid bleaching was desired, the light from a 200 watt projection lamp was allowed to pass through heat filters and fall directly onto the crystal. This produced a decrease of photoconductivity by a factor of a hundred or more in about fifteen minutes.

Since the enhancement could be removed by irradiation with yellow light it was possible to make successive activations with ultraviolet. Four different trials were made, each with ultraviolet radiation of different intensity, the results of which are shown in Fig. 4. The saturation level, that is, the maximum level to which 580 m μ photocurrent could be activated, was the same regardless of the ultraviolet intensity. However, the time required to reach saturation was roughly inversely proportional to the intensity. The time required to reach saturation for the various intensities were: 6.25 μ watts, 6 hours; 12 μ watts, 3 hours; 75 μ watts, 35 minutes; and 125 μ watts, less than 30 minutes.

A decay of the activation similar to that produced by yellow light, but much slower, occurred at room temperature even when the crystal

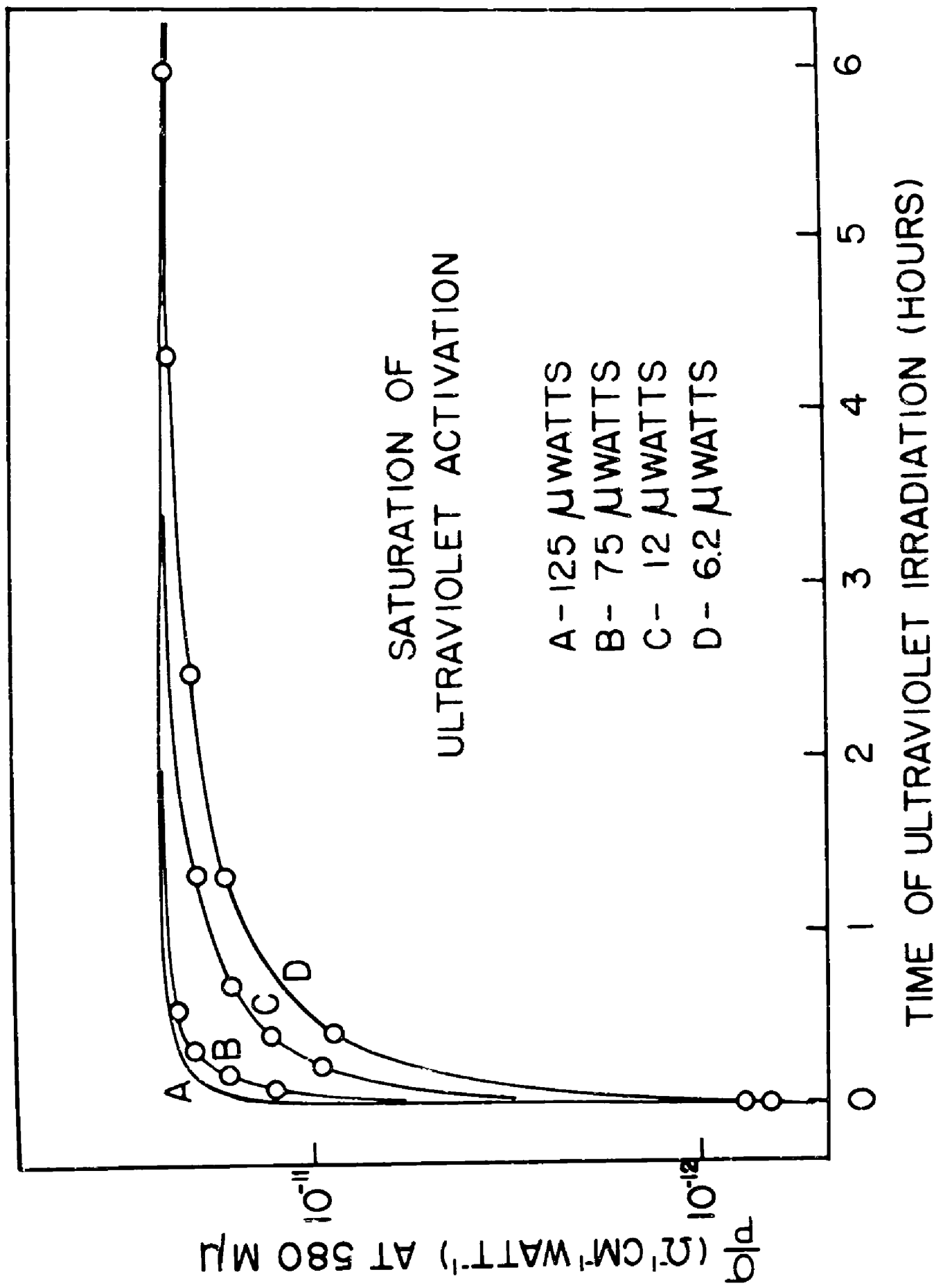


FIG. 4

remained in the dark. The dotted curve in the center of Fig. 3 indicates the small decrease which occurred when the sample remained overnight in the dark. The decay in the dark was accelerated at higher temperatures and the ultraviolet activation disappeared after thirty minutes at 100°C . The explanation is that at higher temperatures more charge carriers can acquire enough thermal energy to become free of their shallow traps and return to the deeper lying levels from which they were originally excited by the ultraviolet radiation. It is not likely that 100°C is high enough to cause any appreciable diffusion of lattice defects, hence the decay of the activation at this temperature must result only from the transport of electrons.

A crystal which had been activated to saturation by ultraviolet irradiation, was heated to about 1000°C in a vacuum better than 10^{-7} millimeters of mercury and cooled slowly to room temperature. After the sample had been vacuum annealed it was found that upon reactivation the photocurrent at 580 m μ saturated at a level which was lower by a factor of four than the previous saturation level. The original saturation level had been reproducible after thermal deactivation at low temperatures (20°C to 100°C) and after deactivation produced by irradiation with yellow light but it could not be reproduced after the high temperature annealing in vacuum. Whereas the decay at low temperature is caused by removing

electrons from traps, the lowering of the saturation level is a completely different effect and must be due to a decrease in the number of traps which may be occupied by the electrons. Therefore it is believed that the level of maximum activation is a measure of the density of defects in the magnesium oxide crystal lattice and that the density of these defects can be changed by annealing the crystal. This conclusion is consistent with the observation that the level of maximum activation is independent of the ultraviolet intensity.

3. Sign of the Charge Carrier

When the photoconductivity was activated by a well defined beam of ultraviolet radiation which did not cover the entire crystal, the enhancement was produced in only the localized region which intercepted the beam. It is believed that the mechanism of enhancement is that the ultraviolet photons produce a transfer of charge carriers from one type of energy level to another. During this transfer, the charge carriers pass through an energy band in which they are free to move under the application of an electric field and thereby give rise to the observed photoconductivity. It was found that by placing a strong electric field across the crystal during the irradiation it was possible to cause the charge carriers to drift a measurable distance in the direction of the electric field before

becoming trapped. This drift was manifested by a shift of the region of enhancement out of the irradiated area in a direction determined by the sign of the charge carrier. A crystal was illuminated by a narrow beam of light passing through it perpendicular to the direction of the applied electric field. The photocurrent was observed for 580 mμ light as the beam of light was moved along the crystal parallel to the direction of the field. Next, with the beam set in the center of the crystal a very narrow region was irradiated for one minute, at 335 mμ, corresponding to one of the ultraviolet bands shown in Fig. 1. This irradiation was sufficient to produce activation but not saturation. Then with 580 mμ light, the beam was again swept across the crystal and the photocurrent was recorded. The results, which are shown in Fig. 5, were found to depend upon the electric field in the crystal at the time of the ultraviolet irradiation. The experiment was performed three times, with no field, and with a field of 3800 volts/cm directed to the right and then to the left. Between trials the previous activation was removed by heating the crystal for several hours at 100°C. In each case where a field was applied the activated region was found to have shifted toward the negative electrode, indicating that the charge carriers are positive, hence they must be holes in the valence band.

An explanation of the enhancement of photoconductivity in the 580 mμ

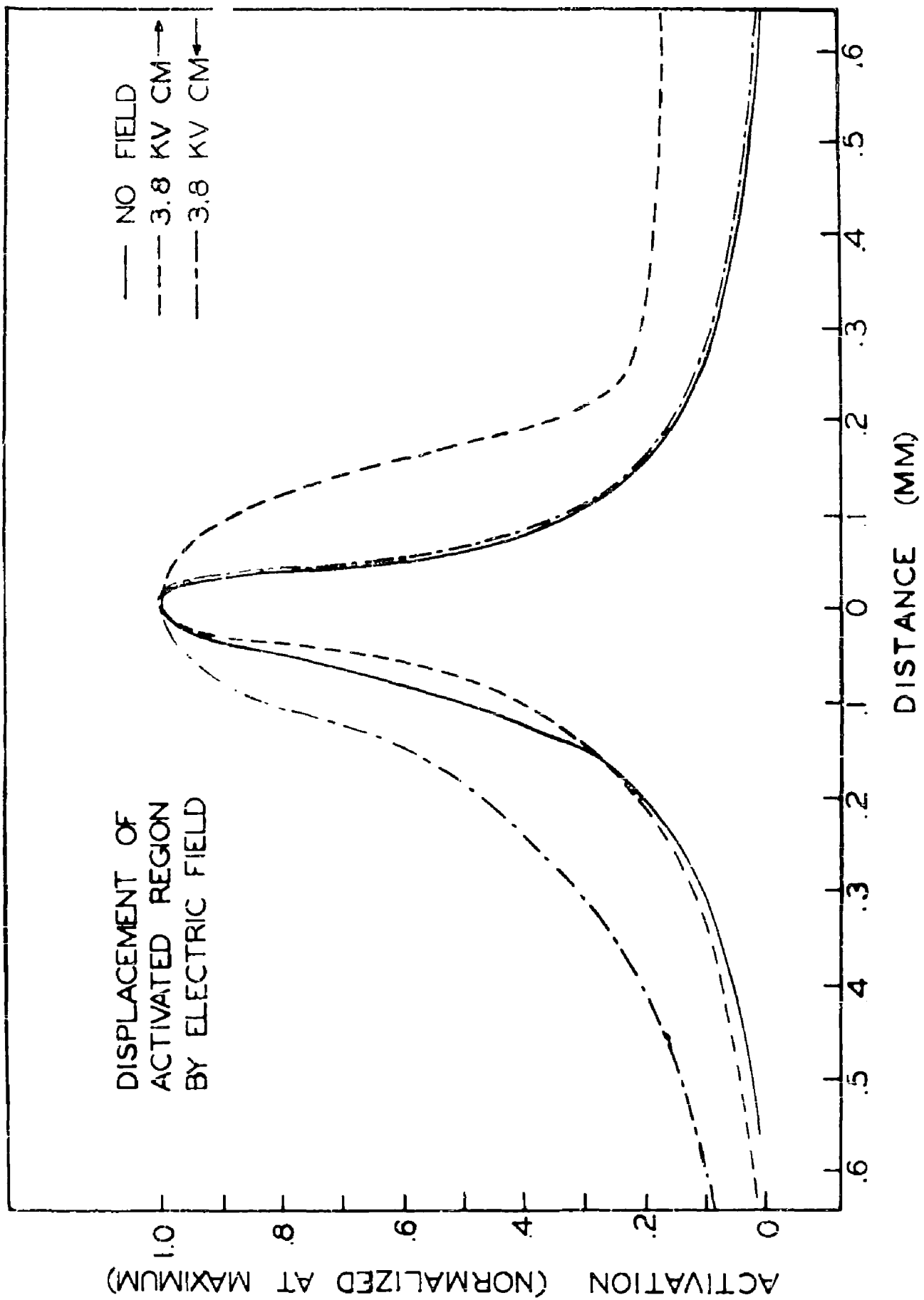


FIG. 5

band by ultraviolet irradiation is that ultraviolet photons excite valence band electrons to unfilled upper levels, in this case to levels 3.7 ev above the valence band. The holes which are produced by this transition migrate until they combine with electrons from the populated levels 2.1 ev above the valence band. It is these vacant levels at 2.1 ev which are now responsible for the optical absorption and photoconductivity bands at 580 m μ . Thermally or optically excited electron transitions to these vacant levels cause a bleaching of the yellow band and a reversal of the process. Electrons from the upper levels may now combine with the holes created in the valence band. This results in the return of the optical absorption and photoconductivity at 335 m μ to their original values. After ultraviolet irradiation the crystal is in a thermodynamically unstable condition, that is, with many higher levels filled and lower lying levels empty. The spontaneous decay of the enhancement is therefore easily understood. Of course, thermal decay occurs during the ultraviolet irradiation and it might seem that the saturation level of the enhancement would be determined by a "rate process" in which the number of vacant low lying traps would be set by an equilibrium between the rate of thermal release of the holes and the rate of their capture. However, there are two objections to this explanation. The first is that the level of saturation is independent of the intensity of ultraviolet radiation. The second is that

if the equilibrium were determined by a rate process the initial rate of decay in the dark should be of the same order of magnitude as the initial rate of increase upon irradiation with ultraviolet. It is apparent from Fig. 3 that this is not the case. It has been mentioned that the photoconductivity in the yellow band increases by a factor of more than a hundred during ultraviolet irradiation while the photoconductivity at the wavelength of irradiation decreases by only a factor of two or three. This can be explained by assuming that there must be a much larger number of upper levels than of low-lying levels. For these reasons it is believed that the saturation is not governed by a rate process and occurs only when all the lower lying levels have become vacant.

4. Neutron Irradiation, Primary Effect

The crystal discussed in connection with Fig. 2 was irradiated with neutrons in the heavy water reactor at the Argonne National Laboratory. After a long irradiation the photoconductivity saturated at the level represented by curve C of Fig. 2, indicating that the maximum level of activation produced by neutrons was a factor of twenty higher than that produced by the ultraviolet irradiation. The sample was left in the dark for several days during which time the photoconductivity decayed to curve B. Because of this rather rapid decay in the dark it is believed that the twenty fold enhancement produced by neutron irradiation was largely

electronic in nature. This activation to a thermally unstable state is referred to arbitrarily as the "primary effect" of neutron irradiation.

A series of irradiations were made in order to determine the rate of activation by neutrons. The neutron induced photoconductivity approaches a saturation and it was found that no further increase was produced by an integrated flux of more than 5×10^{15} neutrons /cm².

A crystal grown at the University of Missouri was neutron irradiated until a saturation of the photoconductivity occurred. The spectral distribution of photoconductivity at saturation is shown by Fig. 6, curve A. This is compared with the spectral distribution of a Norton crystal, curve B, also obtained after saturation by neutron irradiation. Although the curve for the Norton crystal is lower, its peaks are more accentuated than those in the upper curve. These data suggest that the peaks in the photoconductivity curves may be due to one kind of lattice defect and the "background" may be due to other types. The ratios of the densities of defects of the various types would then be different in crystals obtained from the two sources.

The data of Fig. 1 were taken for a crystal immediately after it had been irradiated by neutrons. The four bands were discussed previously.

5. Neutron Irradiation, Secondary Effect

After the photoconductivity of the neutron irradiated crystal of Fig. 2 had decayed from curve C to about the level of curve D, the

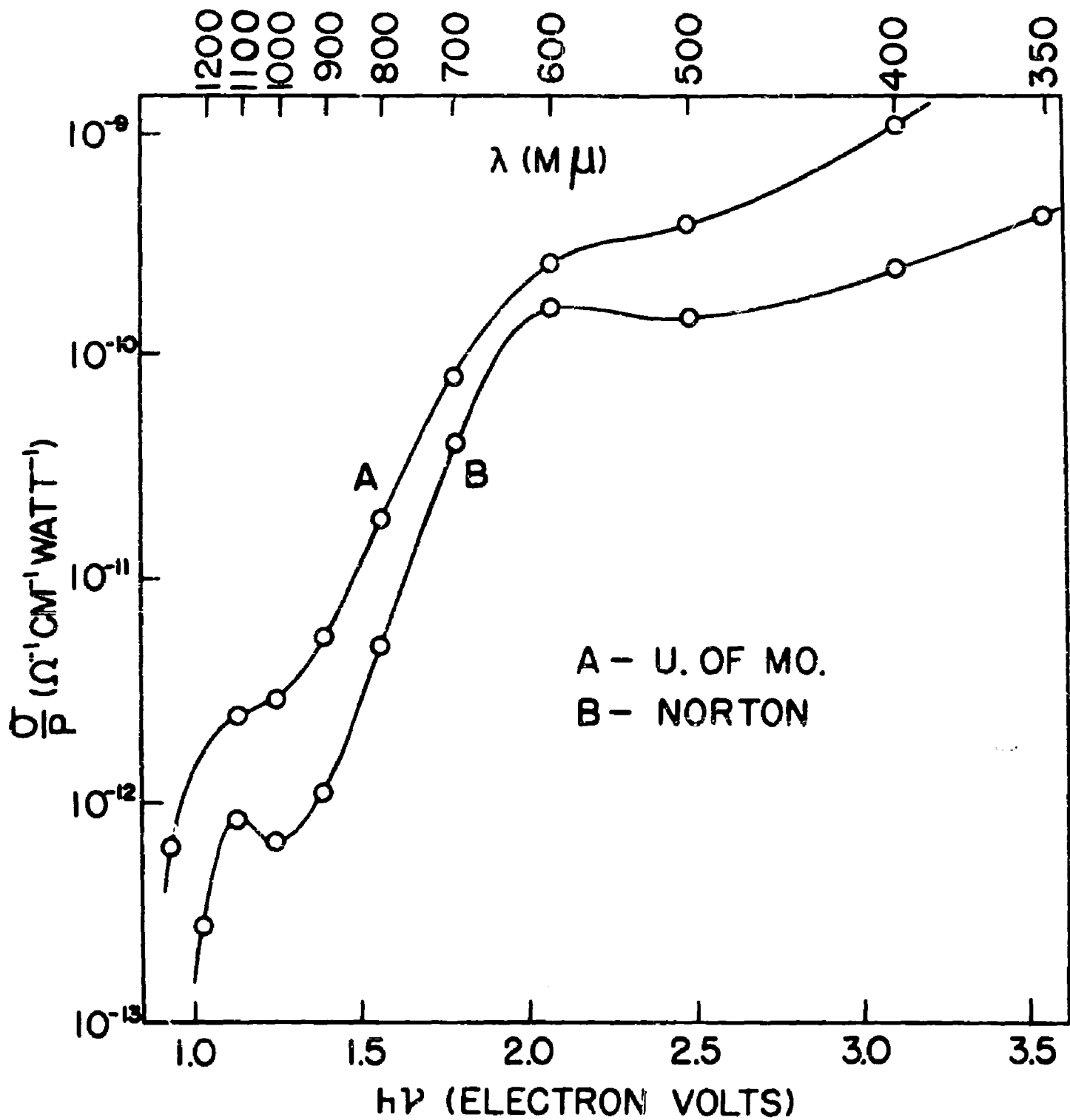


FIG. 6

crystal was irradiated with ultraviolet until saturation occurred. It was found that a new saturation level, curve D, was produced which was higher by a factor of two than the saturation level B observed before the neutron bombardment. If the ultraviolet enhancement saturates only after all the low-lying energy levels are emptied, as suggested earlier, this new saturation level must result from the production of new lattice defects during the neutron irradiation. Thus it is believed that the neutron bombardment produces lattice defects by removing atoms from their normal lattice sites and placing them elsewhere at interstitial positions. As a check on the reproducibility of this effect, the sample was irradiated with 580 mμ light until the photoconductivity had decayed to curve E. Upon subsequent ultraviolet irradiation saturation occurred again at level D, indicating that the new lattice defects produced by the neutron bombardments are stable at room temperature.

This sample was later heated for fifteen hours at 100° C and then irradiated with ultraviolet. The saturation level at 580 mμ was still the same as shown by curve D of Fig. 2. After heating the sample for seventy-five minutes at 300° C the ultraviolet saturation was found to have decreased to the level shown by curve B which represents the condition of the sample before neutron irradiation. The crystal was then irradiated by a neutron flux which was larger by a factor of ten than that used

previously. The integrated neutron flux in this case was 6.5×10^{16} neutrons/cm². The photoconductivity of the sample was at first very high (curve C of Fig. 2) but this "primary effect" could be removed by irradiation with visible light until the sample was in a state near that represented by curve E. Upon subsequent ultraviolet irradiation the photoconductivity measured at 580 mμ saturated at the value shown by curve D, the same as had been obtained after the first neutron bombardment.

The results of the baking procedure and the second neutron irradiation verify the reproducibility of the neutron produced saturation level D and suggest the following: 1. The level of saturation of the enhancement of photoconductivity by ultraviolet irradiation is stable at room temperature and is a measure of the density of defects in the crystal lattice. 2. This level of saturation can be changed by neutron bombardment in a process which shall be called the "secondary effect", as distinguished from the temporary neutron produced enhancement referred to as the "primary effect". 3. The secondary effect itself reaches a saturation level which is independent of the intensity of the neutron flux and which can be reproduced by further bombardment after the crystal has been thermally annealed. 4. The fact that the ultraviolet saturation level can be lowered by heat treatment after the neutron

irradiation indicates that the lattice defects thus produced can be removed by thermal annealing. This supports the hypothesis that neutrons produce lattice defects by knocking atoms from their normal sites rather than by introducing impurities through transmutation.

The secondary effect was investigated further by making a series of short neutron irradiations on a sample grown at the University of Missouri which initially had a much lower ultraviolet saturation level than the other crystals. This crystal was neutron irradiated for a definite time and then exposed to intense radiation in the visible region in order to remove the primary enhancement. The crystal was then irradiated with ultraviolet at 335 mμ until a saturation occurred in the photoconductivity at 580 mμ. This procedure was repeated with irradiation of increasing duration and the results of the experiment are shown in Fig. 7. The curves show that most of the secondary enhancement is produced by an integrated flux, NVT, of 10^{13} neutrons/cm² and only a slight further increase is produced by an irradiation one thousand times longer. The saturation of the secondary effect occurred at the same level for the samples of Fig. 2 and Fig. 7 although before neutron irradiation the saturation levels differed by two orders of magnitude.

A third crystal was studied which initially showed an ultraviolet saturation level the same as the final saturation levels of the other two

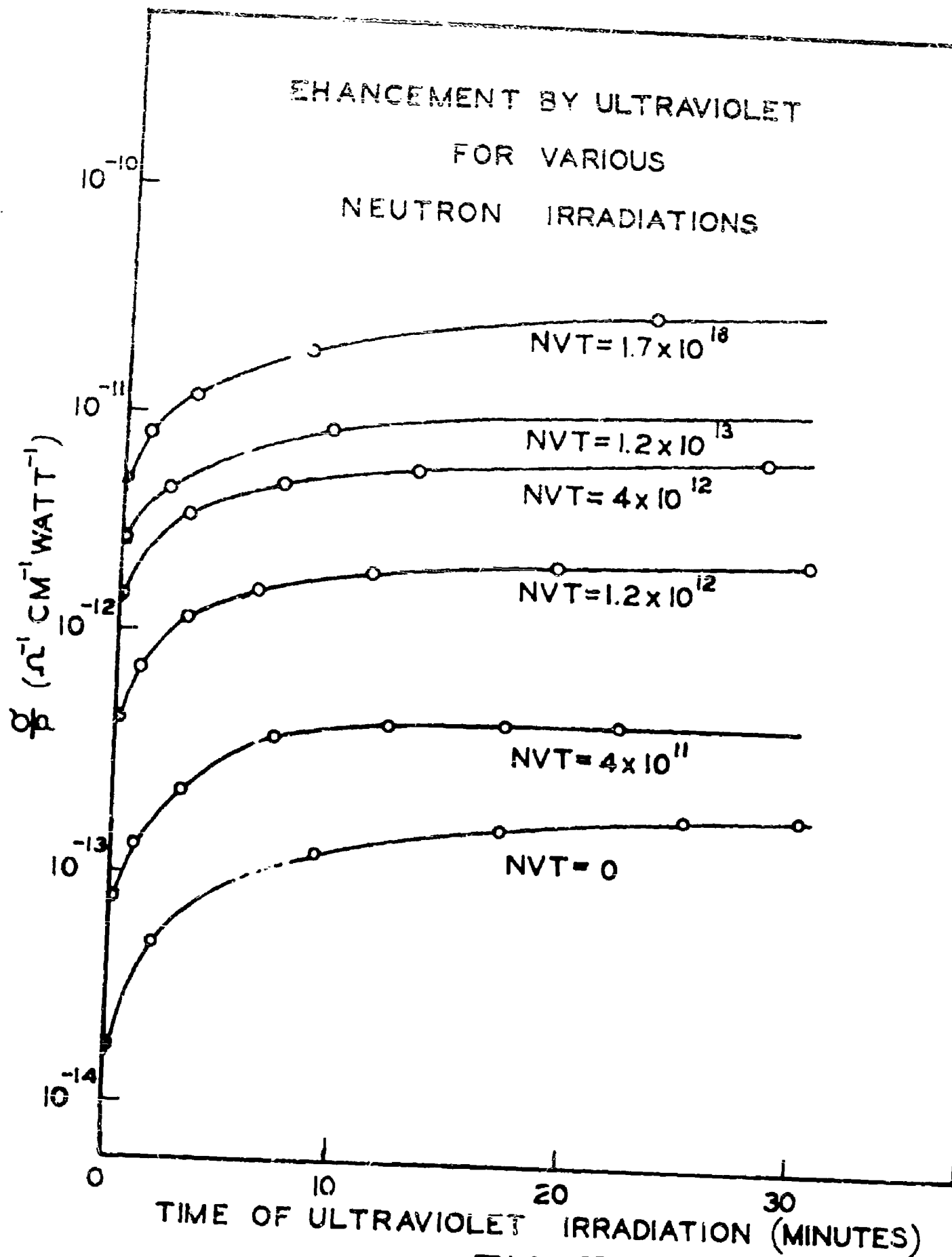


FIG. 7

crystals. When it was irradiated with neutrons no secondary enhancement was observed, that is, the ultraviolet saturation level did not change. Since two of these crystals were obtained from the Norton Company and one was grown at the University of Missouri, these results indicate that the level of saturation of the secondary effect is independent of the origin of the crystals and independent of the original density of lattice defects which were present.

This saturation of the secondary effect results from establishing an equilibrium density of lattice defects by neutron bombardment. That such a density should be reached can be understood by assuming that the energy required to create a vacancy plus an interstitial ion considerably exceeds the activation energy required to cause their recombination. Since both processes are induced by the bombarding neutrons it is clear that an equilibrium density of vacancies might result.

6. Electron Irradiation

Samples which had been irradiated by Van de Graaff electrons showed a purple coloration and a spectral distribution of photoconductivity which were quite similar to those produced by other types of irradiation. A saturation of the enhancement was reached with an irradiation of less than 60 μ amp-seconds of 1 Mev electrons. Because of an extremely rapid decay which occurred at room temperature the time delay between

the end of the irradiation and the measurement of photocurrent was of as great significance as the length of the irradiation; thus the results obtained were somewhat inconclusive.

During the measurement of photoconductivity in electron irradiated crystals it was observed that illumination of the crystal gave rise to a photocurrent even in the absence of an applied potential between the electrodes. The direction of the current was reversible and depended upon the position of the beam of light on the crystal. Regardless of where the beam of light fell on the sample the direction of the current was such that the net flow of electrons was toward the nearer electrode. Thus it is believed that for a short time after the electron bombardment the crystals were negatively charged and because of their extremely high resistivity they were capable of retaining this charge. This trapped charge could create an internal electric field which upon illumination would drive electrons from the crystal to the nearest electrode in the absence of an externally applied potential.

7. Low Temperature Studies

Although only a very small change is observed in the optical absorption bands of magnesium oxide when its temperature is lowered to that of liquid air the photoconductivity was found to decrease by a factor of more than 10^5 between 300°K and 90°K . The sharp dependence

of photoconductivity upon temperature suggests that a two-step process may be involved in which the release of charge carriers depends upon their acquiring enough thermal energy to be released from localized energy levels to which they have been excited by the photons.

8. Compressed Pills

Gold electrodes were evaporated on the surfaces of several pills of compressed magnesium oxide powder having a density approximately one-half of the crystal density. The magnesium oxide powder from which these pills were formed was the same as used for the crystals grown in this laboratory. Any differences in the observed results for the single crystals and the compressed pills must result from either a difference in physical structure or to impurities entering during the growth of the crystals. Although a photocurrent could be detected, it was found that the dark current present in a compressed pill was about a million times greater than in a single crystal of similar dimensions. Hence the spectral dependence of photoconductivity could not be measured. All attempts to reduce the dark current by baking the samples at 100° C and by leaving them in the desiccated sample box for long periods of time were unsuccessful. This suggests that the dark current is a surface property and is much larger in the pills because of the large surface area.

IV DISCUSSION OF RESULTS

1. Photoconductivity Bands

Measurements of the spectral distribution of photoconductivity in magnesium oxide have revealed bands which correspond in wavelength to those which were found in the optical absorption spectra by other investigators. The photoconductivity study has shown that electronic transitions are possible at 1.2, 2.1, 3.7 and 4.8 ev.

The additive coloration experiments of Weber⁵ have identified the absorption bands at 2.1, 3.7, and 4.8 ev with excess magnesium and two bands at 4.3 and 5.7 ev with excess oxygen. Since it is believed that neutron bombardment displaces atoms from their normal lattice sites to interstitial position creating vacancies both excess magnesium and excess oxygen absorption bands might be produced by the neutron irradiation. The photoconductivity bands which were found after irradiation correspond to the optical absorption bands due to excess magnesium and bands due to the excess oxygen were not detected. The 4.3 ev oxygen band may have been present but obscured by the two adjacent 3.7 and 4.8 ev magnesium bands. The 5.6 ev band was not observed because equipment limitations prevented measurements at that photon energy.

2. Energy Level Model

A fairly definite energy level model can be reduced from these

transitions and the results of the various experiments. This model is shown in Fig. 8. The width of the forbidden band is not known but it is certainly larger than 6.5 ev because at that energy the coefficient of optical absorption is still fairly small. Photon energies capable of inducing band to band transitions should give rise to absorption coefficients larger by a factor of 10^3 or 10^4 than is observed at 6.5 ev. On the basis of x-ray measurements¹⁰ the forbidden gap may be as large as 10 to 15 ev. Electrons play the major role in electrical conduction at high temperatures (1300°K) as indicated by thermoelectric power measurements.¹¹ It has also been found that the thermionic work function of magnesium oxide is about 2.8 electron volts¹², but its relation to the energy level model is uncertain as yet.

An experiment was described which showed that holes are produced by irradiation at 335 mμ and 580 mμ. Localized levels must lie at several energies above the valence band corresponding to the observed photoconductivity bands. For the sake of simplicity only two of these are shown in Fig. 8-A, at 2.1 and 3.7 ev above the valence band. Initially, most of the E_2 levels are filled by electrons in accord with a Fermi-Dirac distribution function and many of the E_1 levels are vacant. When the

10. Mott and Gurney, p. 76-78, 101

11. H. F. John, Private Communication

12. J. R. Stevenson, O.N.R. Quarterly Progress Report, Dept. of Physics, University of Missouri (June 15, 1952)

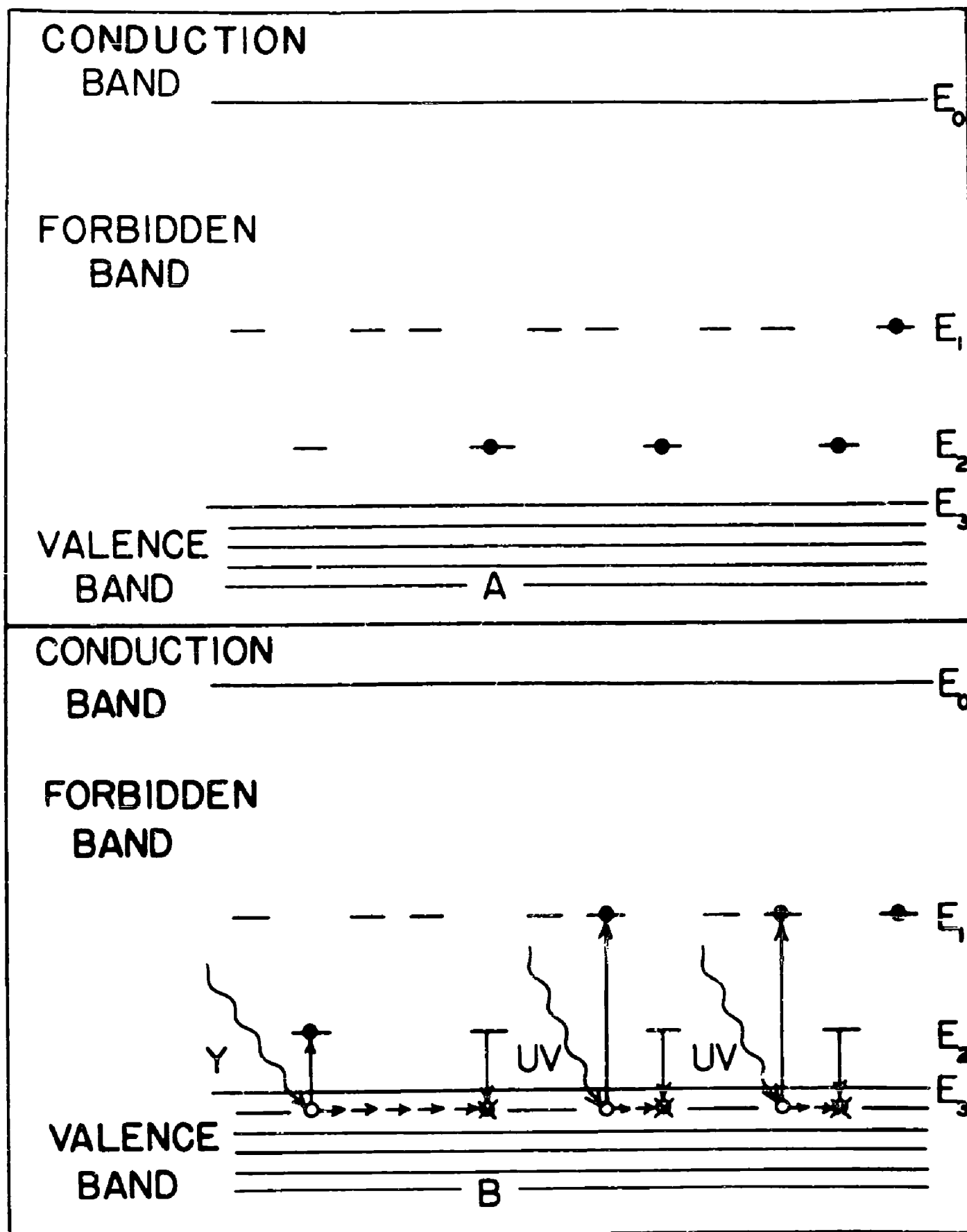


FIG. 8

crystal is illuminated by 530 mμ light, very few E_2 levels can accept electrons excited from the valence band hence the optical absorption and photoconductivity are weak at that wavelength. However, where there is a vacant E_2 level an electron can be excited to it (quantum Y in Fig. 8-B) producing a hole in the valence band. This hole then drifts with the electric field until it captures an electron from one of the filled levels in the forbidden band, thus accounting for the weak photoconductivity initially present. Since there are many unfilled levels at E_1 the optical absorption coefficient is high for photon energies capable of producing this transition.

The process of enhancement of photoconductivity in the yellow region by irradiation with ultraviolet light can be explained by this model. Ultraviolet photons, quanta UV in Fig. 8-B, excite electrons to levels at E_1 , creating holes in the valence band. These holes then drift until they combine with electrons from levels at E_2 . There are now many empty E_2 levels so that upon subsequent irradiation with yellow light the probability of electron transitions to those levels is larger than before and the crystal will exhibit both a greater optical absorption and photoconductivity at that energy. The activation process continues until all of the E_2 levels are empty and a saturation of the enhancement occurs. Of course, holes drifting through the valence band may capture electrons from other energy

levels but only the capture from the 2.1 ev level need be considered to explain the enhancement at 580 m μ .

The band at 1050 m μ or 1.2 ev is also enhanced by irradiation at 335 m μ . The 1.2 and 2.1 ev bands increase simultaneously upon ultraviolet irradiation and both bands reach a saturation at about the same time. Since both bands are activated by the same wavelength the charge carriers associated with the 1.2 ev levels must be holes in the valence band as they are for the 2.1 ev levels. These bands can also be activated by irradiation with ultraviolet at wavelengths other than 335 m μ . The same process explains the enhancement produced by the other wavelengths and the apparent equivalence of these various wavelengths suggests that all photoconduction in magnesium oxide is by means of holes in the valence band.

When a crystal is activated electrons are transferred from the E_2 levels via the valence band to the levels at E_1 . The probability of a transition from the valence band to an E_1 level is therefore diminished, accounting for the decrease with time in the photocurrent produced by the irradiating wavelength. The fact that this decrease is only a factor of two compared to the much larger increase of the E_2 photoconductivity band is explained by assuming that there are many more levels at E_1 than at E_2 .

In the state of activation produced by ultraviolet irradiation the distribution of electrons among the energy levels is not thermally stable because there are many more electrons at the higher energy, E_1 , than there are at E_2 . Decay to the original state takes place by a mechanism in which an electron in the valence band is thermally excited to the E_2 level. This creates a hole in the valence band which drifts until it captures an electron from a filled E_1 level. The net effect is the transfer of electrons from the E_1 levels to the E_2 levels by "passing through" the valence band. Since the E_2 levels in this case are 2.1 ev above the valence band, there is small probability that electrons will acquire enough thermal energy to make the transition, thus the decay occurs slowly at room temperature. However, if photons of this energy irradiate the crystal the rate of transfer of electrons to the E_2 levels is increased and the photoconductivity at that wavelength decays much more rapidly.

3. Range

In the experiment determining the sign of the charge carrier, the crystal is irradiated in a very narrow region by ultraviolet light. This produces charge carriers which drift, on the average, a small distance down the potential gradient before being trapped. A very rough idea of the range can be obtained by noting this distance of drift. With an electric field of 3.8×10^3 volts/cm the displacement of the region of activation

can be estimated from Fig. 5 to be about 5×10^{-3} cm. Most of the photoconductivity experiments were performed with a field of 1 kV/cm in which case the range would be on the order of 10^{-3} cm.

4. Quantum Efficiency

If n charge carriers are created and trapped in the times t , each moving a distance x before being trapped, the photoconductivity current indicated by an external detector is,

$$i = \frac{nex}{tL} \quad (1)$$

If radiation of frequency γ falls on the crystal for the time t , the number of photons absorbed is,

$$N = \frac{Pt}{h\gamma} \quad (2)$$

where P is the optical power absorbed in the crystal. Solving equation (1) for n and writing the fraction n/N one obtains the quantum efficiency,

$$\frac{n}{N} = \frac{Li\gamma}{xeP} \quad (3)$$

independent of any assumption of the lifetime. Substitution of values for a typical sample shows that n/N increases from 10^{-7} electrons/photon at 1050 m μ to 10^{-4} electrons per photon at 255 m μ . These efficiencies are small but are not unreasonable considering the extremely low conductivity of magnesium oxide. For comparison, the quantum efficiency

for photoemission from barium oxide¹³ is only about 10^{-6} electrons per photon at 600 m μ .

5. Density of the Color Centers

Using the value 10^{-4} electrons/photon for the quantum efficiency at the wavelength of the ultraviolet irradiation and knowing the time required to saturate the photoconductivity at 580 m μ , one can calculate the number of electrons required to fill all of the 2.1 ev levels. The number of electrons released during the time, T, required to produce this saturation is,

$$n = \left(\frac{n}{N} \right) \frac{PT}{h\nu} = \rho V \quad (4)$$

where ρ is the density of centers and V is the volume of the crystal irradiated. From this calculation one finds there are about 2×10^{14} centers/cm³. This calculation was carried out for the crystal of Fig. 2 following neutron irradiation and represents the saturation level of 2.1 ev centers, E_2 of Fig. 8. Since the 1.2 ev band saturated in about the same time as the 2.1 ev band, approximately the same density of centers must be associated with that energy.

In terms of other physical quantities, the range per unit field strength,

$$\frac{x}{F} \propto \frac{1}{\rho} \quad (5)$$

where l is the mean free path for collisions with the lattice and ρ is

13. I. L. Sparks, Thesis, University of Missouri, 1951

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